We know that the strength of metallic bonding is roughly related with the number of unpaired electrons present in the valence-shell of the element. In general, greater in the number of unpaired electrons, stronger is the metallic bonding and hence greater is the melting point of the element. As we move along a particular series, since the number of unpaired electrons increases upto Cr (in 1st series), Mo (in 2nd series) and W (in 3rd series), the melting points of the elements also increase upto these elements and then with decrease in the number of unpaired electrons, the melting points also decrease. Since Zn, Cd and Hg donot have any unpaired electrons, their melting points are the lowest in their respective periods. Their melting points are so low that these elements can be volatilised off easily. In fact, Hg is a liquid at room temperature.

$\Rightarrow$ Although Mn, Tc and Re also have the maximum number of unpaired electrons, these elements have lower values of their melting points than Cr, Mo and W respectively. Their low values are due to the fact that the metallic bonding in these elements are relatively weak.

6. Ionisation energies

The values of first ionisation energy (in kJ/mole) of 1st, 2nd and 3rd transition series elements are given in Table 6.6. From this table the following points may be noted:

(*i*) The values of ionisation energy increase as we move from left to right in each series, although the increase is not quite regular, *i.e.*, the increase in ionisation energies is quite gradual or slow. The reason for the gradual increase is given below.

Explanation. We know that when we move from left to right in a given series, the nuclear charge increases. The increased nuclear charge would attract the ns^2 electron cloud with greater force and hence the ionisation energies are expected to increase at each step. However, as the electron is added to $(n-1)d$ sub-shell at each next element, the ns^2 electrons are shielded more and more. The effect of increasing nuclear charge is opposed by the additional screening effect of the nucleus and consequently, the ionisation energies increase but quite slowly along a given series.

Table 6.6. *Ionisation energies (kJ mol^{-1}) of d-block elements*

These values have been taken from Table 2.2A, page 40-42, "*Inorganic Chemistry: Principles of Structure and Reactivity*" (2nd edition) by James E. Huheey.

Groups →	IIIB (3)		IVB (4)	VB (5)	VIB (6)	VIIB (7)	←VIII→ (8)	(9)	(10)	IB (11)	IIB (12)
1st or 3d series (4th period) →	Sc_{21} 631		Ti_{22} 658	V_{23} 650	Cr_{24} 652.8	Mn_{25} 717.4	Fe_{26} 759.4	Co_{27} 758	Ni_{28} 736.6	Cu_{29} 745.5	Zn_{30} 906.4
2nd or 4d series (5th period) →	Y_{39} 616		Zr_{40} 660	Nb_{41} 664	Mo_{42} 685	Tc_{43} 702	Ru_{44} 711	Rh_{45} 720	Pd_{46} 805	Ag_{47} 731	Cd_{48} 867.7
3rd or 5d series (6th period) →	La_{57} 538.1	(Ce_{58}—Lu_{71})	Hf_{72} 654	Ta_{73} 761	W_{74} 770	Re_{75} 760	Os_{76} 840	Ir_{77} 880	Pt_{78} 870	Au_{79} 890.1	Hg_{80} 1007

$\Rightarrow$ (*ii*) When we proceed from top to bottom in group III B, ionisation energy values decrease as $Sc_{21} > Y_{39} > La_{57}$. However, in most of the remaining groups the ionisation energies increase in the same direction, *i.e.*, the ionisation energies of the elements lying after La_{57} in 3rd series are greater than those of their corresponding elements lying in 1st and 2nd series.

Explanation. In the atoms of 14 elements following La_{57} (Ce_{58} to Lu_{71}), 4*f* orbitals are completely filled and hence cannot shield the nucleus effectively. Due to ineffective (*i.e.*, poor) shielding of the nucleus by the 4*f* electrons, the elements lying after La_{57} in 3rd series have greater effective nuclear charge acting on the ns^2 elctrons. Therefore, the ionisation energies of the elements following La_{57} in 3rd series are higher than those of their corresponding elements lying in 1st and 2nd series.

Group - II B

(*iii*) In each series the elements of group II B (Zn, Cd and Hg) have the highest values for their ionisation energy. This is due to the extra stability associated with their completely-filled $(n-1)d$ and ns orbitals ($Zn_{30} = 3d^{10}\ 4s^2$, $Cd_{48} = 4d^{10}\ 5s^2$ and $Hg_{80} = 5d^{10}\ 6s^2$).

(*iv*) When we compare these values of *d*-block elements with those of *s*-and *p*-block elements, we find that these values are higher than those of *s*-block elements but lower than those of *p*-block elements. It is also seen that in any particular series, the difference in ionisation energies between any two successive *d*-block elements is much less as compared to the difference in case of successive *s*-block or *p*-block elements.

Relation between the ionisation energy and stability of a metal in a given oxidation state

With the help of ionisation energy values we can predict which of the two metals in a given oxidation state is thermodynamically more stable. As an example let us compare the relative stability of Ni (II)—Pt(II) and Ni(IV)—Pt(IV) pairs. When a metal, M(0) is converted into M(II), energy required for this conversion is equal to the sum of 1st (I_1) and 2nd (I_2) ionisation energies of the metal. Similarly when a metal, M(0) is converted into M(IV), energy required is equal to the sum of I_1, I_2, I_3 and I_4 of the metal. Thus :

$$\text{Ni(0)} \xrightarrow{-2e^-} \text{Ni (II), Energy required} = I_1 + I_2 = \underline{2.49} \times 10^3 \text{ KJ mol}^{-1}$$ stable

$$\text{Pt(0)} \xrightarrow{-2e^-} \text{Pt (II), Energy required} = I_1 + I_2 = \underline{2.66} \times 10^3 \text{ KJ mol}^{-1}$$ unstable

$$\text{Ni(0)} \xrightarrow{-4e^-} \text{Ni (IV), Energy required} = I_1 + I_2 + I_3 + I_4 = 11.29 \times 10^3 \text{ KJ mol}^{-1}$$

$$\text{Pt(0)} \xrightarrow{-4e^-} \text{Pt (IV), Energy required} = I_1 + I_2 + I_3 + I_4 = \underline{9.36} \times 10^3 \text{ KJ mol}^{-1}$$

The above values show that since ($I_1 + I_2$) for Ni(II) is less than ($I_1 + I_2$) for Pt(II), Ni(II) compounds are more stable than Pt(II) compounds. Similarly since the value of ($I_1 + I_2 + I_3 + I_4$) for Pt (IV) is less than that for Ni(IV), Pt(IV) compounds are more stable than Ni(IV) compounds. This fact becomes evident when we find that $K_2[PtCl_6]$ is a well known compound of Pt(IV) but the corresponding compound of Ni (IV) (*i.e.*, K_2NiCl_6) does not exist at all.

7. Standard reduction potential values

These values (in volts) for the elements of 1st transition series are given below:

Elements	V	Cr	Mn	Fe	Co	Ni	Cu
E^o_{red} *(volts)*	− 1.18	− 0.91	− 1.18	− 0.44	− 0.28	− 0.25	+ 0.34

These values are for the reduction reaction, $M^{2+}(aq) + 2e^- \rightleftharpoons M(s)$.

It may be seen that these values, except for Cu, are negative and there is no regular trend in these values, since the ionisation energies ($I_1 + I_2$) and sublimation energies of these metals donot show any regular trend. These values have been used to explain the reducing property and reactivity of these metals.

8. Variable oxidation states

With the exception of a few elements, most of the *d*-block elements show more than one oxidation state (*i.e.*, variable or several oxidation states). The following two reasons have been given to explain why *d*-block elements show several oxidation states:

(*i*) $(n-1)d$ and ns orbitals in the atoms of *d*-block elements have almost the same energies and hence electrons can be removed from $(n-1)d$ orbitals as easily as they can be removed from ns orbital.

(*ii*) After removing ns electron(s) the remainder is called *core* or *kernel* (penultimate shell).

[illegible]

unstability of core

In case of most of the *d*-block elements, the core is unstable and hence can lose one or more electrons, resulting in the formation of cations having different oxidation states, *i.e.*, the removal of one or more electrons from the unstable core gives several oxidation states to transition metals.

Various oxidation states shown by transition elements are given in Table 6.7. Oxidation states shown in bracket are unstable oxidation states.

Table 6.7. *Various oxidation states of transition metals. Unstable oxidation states are shown in bracket.*

Elements of 1st transition series (3*d*-series) (n = No. of unpaired electrons)

Sc	$3d^14s^2$	($n = 1$)	+2, +3
Ti	$3d^24s^2$	($n = 2$)	(0, −1), +2, +3, +4
V	$3d^34s^2$	($n = 3$)	(−1, 0, +1), +2, +3, +4, +5
Cr	$3d^54s^1$	($n = 6$)	(0, +1), +2, +3, (+4, +5), +6
Mn	$3d^54s^2$	($n = 5$)	(−1, 0, +1),+2, +3, +4, (+5), +6, +7
Fe	$3d^64s^2$	($n = 4$)	(−2, 0, +1), +2, +3, (+4, +5, +6)
Co	$3d^74s^2$	($n = 3$)	(−1, 0, +1), +2, +3, (+4)
Ni	$3d^84s^2$	($n = 2$)	(0, +1), +2, +3, +4
Cu	$3d^{10}4s^1$	($n = 1$)	+1, +2, (+3)
Zn	$3d^{10}4s^2$	($n = 0$)	+2

Elements of 2nd transition series (4*d*-series)

Y	+3
Zr	(0, + 3), +4
Nb	(−1, 0, +1, +2, +3, +4), +5
Mo	(0, +1), +2, +3, +4, +5, +6
Tc	(0), +2, (+3, +4, +5, +6, +7)
Ru	(0), +2, +3, +4, (+5, +6, +7, +8)
Rh	(0, + 1), +2, +3, +4, (+6)
Pd	(0), +2, (+3), +4
Ag	+1, (+2, +3)
Cd	+2

Elements of 3rd transition series (5*d*- series)

La	+3
Hf	(+3), +4
Ta	(−1, +1, +2, +3, +4), +5
W	(0, +1), +2, (+3), +4, +5, +6
Re	(−1, 0, +1, +2), +3, +4, +5, (+6), +7
Os	(0), +2, +3, +4, (+5), +6, (+7), +8
Ir	(0, + 1), +2, +3, +4, (+6)
Pt	(0), +2, (+3), +4, (+5, +6)
Au	+1, +3
Hg	+1, +2

Oxidation states shown by *d*-block elements of 1st transition series

In connection with the oxidation states exhibited by the *d*-block elements of 1st transition series the following points may be noted:

(i) +1 and +2 oxidation states. The oxidation states shown in bracket are unstable oxi states. These are low oxidation states. The remaining oxidation states are stable. Out of the stable oxidation states, +1 is the lowest oxidation state for Cu while for other elements the lowest oxidation state is +2. Cr and Cu both show +2 oxidation state when one 4*s* and one 3d electrons are lost while the remaining elements exhibit this oxidation state (*i.e.* +2 state) when both *ns* electrons are involved in bonding.

= Cu →
Cu = +2.

(ii) Stabilisation of unstable (low) oxidation states. It may be seen that the low oxidation states like −1, 0, +1 are unstable. These states are stabilised by forming complexes with π-acid ligands like CO, NO, N_2, PR_3, AsR_3, CNR (isocyanide), CN^-, C_6H_6, toluene, α, α′-dipyridyl, o-phenanthroline, ethylene etc. These ligands are electron-deficient, since they have vacant π-orbitals, called acceptor orbitals. In addition to vacant π-orbitals, they also have filled orbitals. called donor orbitals. Thus these ligands have vacant π-acceptor orbitals as well as filled donor orbitals. These ligands can stabilise transition metal atoms in their low oxidation states (*e.g.* +1, 0, −1) by forming complexes with them. The complexes formed have double bonding which can be represented as $L \rightleftharpoons M$. This double bonding indicates that in these complexes both the metal and the ligand act both as donors and acceptors. How L → Mσ and L ← Mπ bonds are formed has been explained below.

The donor orbital on the ligand overlaps with the vacant orbital on transition metal atom in low oxidation state and forms a L →Mσ bond. The formation of L → Mσ bond accumulates negative charge on the transition metal atom. The accumulation of negative charge leads to substantial repulsion between the negative charges of the metal and of the ligands. In order to decrease the magnitude of the negative charge accumulated on the metal atom, suitable filled *d*-orbital on the metal atom overlaps with the vacant π-orbital (acceptor orbital) on the ligand. This type of overlap transfers some negative charge from the metal to the ligand and M → Lπ bond is formed. Thus the vacant π-orbital of the ligand receives the back-donated electrons from the filled *d*-orbitals on the transition metal and thus stabilises the metal atom in lower oxidation state. Thus we have double bonding between the ligand and the metal atom. One is a L → Mσ bond and the other is a M → Lπ bond. The complexes formed are called *π-acid complexes*, since M → Lπ bond is formed in these complexes. In the formation of M → Lπ bond, since the ligand accepts the back-donated electrons from the metal into its vacant π-orbitals, the ligand is said to behave as a π-acid and hence is called *π-acid ligand* or *π-bonding ligand*. Examples of some complex compounds formed by transition metal atoms in their low oxidation states (+1, 0, −1) with π-acid ligands like CO, CNR, C_6H_6, PCl_3 etc. are $[Cr^0(CO)_6]^0$, $[Cr(CNR)_6]^0$, $[Cr^0(C_6H_6)_2]^0$, $[Cr^{+1}(C_6H_6)_2]^+$, $[Fe^0(CO)_5]^0$, $[Co^0_2(CO)_8]^0$, $Na^+[Co^{-1}(CO)_4]$, $[Ni^0(Co)_4]^0$, $[Ni^0(CNR)_4]^0$, $[Ni^0(PCl_3)_4]^0$, $Na^+[V^{-1}(CO)_6]$, $[V^0(dipy)_3]^0$, $[V^{+1}(dipy)_3]$].

It may easily be understood that in order to get $L \underset{\pi}{\overset{\sigma}{\rightleftharpoons}} M$ bond, transition metal in its lower oxidation state should have both vacant as well as filled *d*-orbitals.

(iii) High oxidation state. The highest (maximum) oxidation state for the first five elements (Sc to Mn) is equal to the sum of the electrons in 4*s* and 3*d* orbitals. On the other hand, the highest oxidation state for the remaining five elements (Fe to Zn) is not equal to the sum of the electrons in 4*s* and 3*d* orbitals.

The high oxidation states of many transition metals like V(V), Cr(VI), Mn(IV), Mn(VII), Fe(III), Fe(VI), Co(III), Ni(III), Cu(III), Ag(II), Ag(III) etc. are oxidising (*i.e.*, unstable). These unstable oxidation states which are high oxidation states get stabilised by forming complexes with small highly electronegative ligands like O^{2-}, F^-, Cl^-, per iodate (IO_6^{5-}), tellurate (TeO_6^{6-}) etc. Examples are given below:

(*a*) O^{2-} ion stabilises Fe(VI), V(V), Cr(VI) and Mn(VII) by forming FeO_4^{2-} (ferrate),

VO_4^{3-} (vanadate), CrO_4^{2-} (chromate) and MnO_4^{2-} (permanganate) ions respectively. FeO_4^{2-} is obtained by the anodic oxidation of $Fe(OH)_3$ in conc. alkali.

(*b*) V(V) is stabilised by F^- ion by forming VF_5 (but not VCl_5 and VBr_5).

(*c*) IO_6^{5-} and TeO_6^{6-} ions stabilise Ag (III) by forming the complex compounds namely $M_7^+[Ag^{3+}(IO_6)_2].xH_2O$ and $M_9^+[Ag^{3+}(TeO_6)_2].xH_2O$ respectively. TeO_6^{6-} also stabilises Cu(III) by forming $M_9^+[Cu^{3+}(TeO_6)_2].xH_2O$. All these complexes are obtained in alkaline medium. IO_6^{5-} and TeO_6^{6-} also stablise Mn(IV) by forming the red-coloured complex compounds namely $Na_7H_4[Mn^{+4}(IO_6)_3].7H_2O$ and $K_7H_4[Mn^{+4}(IO_6)_3].8H_2O$. These complexes are obtained by the alkaline oxidation of $MnCl_2$ in presence of sodium (or potassium) periodate. $Na_2H_3IO_6$ (or $K_2H_3IO_6$). Alkaline oxidation of $MnCl_2$ in presence of sodium (or potassium) tellurate gives dark red $Na_7H_7[Mn^{+4}(TeO_6)_3].3H_2O$ or $K_6H_8[Mn^{+4}(TeO_6)_3].5H_2O$ ($\mu = 3.30$ B.M.).

(*d*) Ag(II) has been stabilised by forming complexes with *pic*⁻, *py*, *dipy* and *o-phen*. The composition of the complexes formed are $[Ag^{2+}(pic)_2]^0$, $[Ag^{2+}(py)_4]^{2+}$, $[Ag^{2+}(dipy)_2]^{2+}$ and $[Ag^{2+}(o\text{-}phen)]^{2+}$ respectively. Ag(III) has been stabilised by forming the complex with *big*H. The composition of the complex compound is $[Ag^{3+}(bigH)_2](OH)(SO_4)$ (silky crystals).

(*e*) In aqueous solution high oxidation states are favoured in alkaline medium. Thus in order to stabilise the lower oxidation states in aqueous solution non-oxidising acids should be used. Transition metal hydroxides are usually oxidised by atmospheric oxygen, *e.g.*, pale green $Fe(OH)_2$ gets oxidised to brown $Fe(OH)_3$ on standing in air.

(*f*) F^- and O^{2-} ions can form compounds in which Fe and Co achieve oxidation states greater than +3 or Ni and Cu acquire oxidation state greater than +2.

(*iv*) **Ionic/covalent character of compounds of a given transition metal in various oxidation states.** With the increase in the oxidation state of a given transition metal, the covalent character of its compounds increases. Thus the compounds of a given transition metal in lower oxidation states are ionic while those of the same metal in high oxidation states are covalent, *e.g.* $\overset{+2}{V}Cl_2$ is ionic, $\overset{+3}{V}Cl_3$ is less ionic while $\overset{+4}{V}Cl_4$ is covalent.

Explanation. As the oxidation state of the transition metal increases, the charge density on the metal also increases. This results in the increase of the polarisation of the anion charge cloud by the metal and hence covalent character increases (see *Fajan's Rules*).

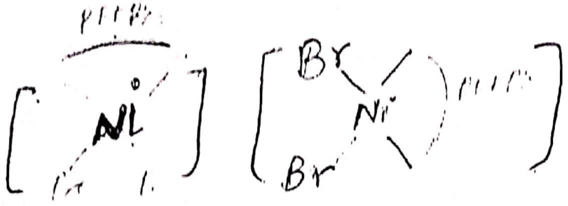
(*v*) **Acidic/basic character of the compounds of a given transition metal in various oxidation states.** We have said earlier that with the increase in the oxidation state of a given transition metal, the covalent character of its compounds increases. The increase in the covalent character also increases the acidic character of the compound. Thus the compounds of a given transition metal becomes more and more acidic as the oxidation state of the transition metal increases. This fact becomes evident when we study the following :

(*a*) The variation of the basic, amphoteric and acidic character of the oxides of V, Cr and Mn is as shown below :

(*i*) *Oxides of vanadium :*	VO	V_2O_3	VO_2	V_2O_5
Oxidation state of vanadium :	+2	+3	+4	+5
Nature of the oxides :	Basic	Basic	Amphoteric	Acidic

(*ii*) *Oxides of Cr :*	CrO	Cr_2O_3	CrO_2	CrO_3
Oxidation state of Cr :	+2	+3	+4	+6
Nature of the oxides :	Basic	Amphoteric	Amphoteric	Acidic

(3) PKa ⇒ pKaH



Coordination Isom. Same molecular formula but diff. orientation around the metal atom

15

CHAPTER

Isomerism in Coordination Compounds

Introduction

The coordination compounds which have the same molecular formula but have their ligands attached to the central metal atom in different ways are called **isomers**. These isomers have different properties. The phenomenon that gives rise to different isomers is called **isomerism**.

Isomerism may be of two types viz., *structural isomerism* and *stereo (space) isomerism*.

Structure of complex comp.

Structural Isomerism

This isomerism arises due to the difference in the structures of complex (coordination) compounds. This isomerism is of the following types:

1. Conformation Isomerism

In this isomerism two isomers have different geometries but are otherwise identical. For example, $[Ni^{2+}(P.Et.Ph_2)_2Br_2]$ complex (four-coordinated complex) gives two conformation isomers. One of these is green and paramagnetic while the other is brown and diamagnetic. The green form is tetrahedral while the brown form is square planar. Thus these have different geometries but the coordination number of Ni^{2+} ion in both the isomers is the same (=4).

2. Ionisation Isomerism

The complex compounds showing ionisation isomerism are called *ionisation isomers*. These isomers have the same molecular formulae and are produced when the ligands given in the coordination sphere and the anions present outside the coordination sphere are exchanged with each other. Thus both the complex compounds of each of the following pairs are ionisation isomers to each other.

(i) $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5(SO_4)]Br$

(ii) $[Co(NH_3)_4Cl_2]NO_2$ and $[Co(NH_3)_4Cl(NO_2)]Cl$

(iii) $[Pt(NH_3)_4Cl_2]Br_2$ and $[Pt(NH_3)_4Br_2]Cl_2$

(iv) $[Co(NH_3)_5(NO_3)]SO_4$ and $[Co(NH_3)_5(SO_4)]NO_3$

(v) $[Cr(NH_3)_4I_2]Br$ and $[Cr(NH_3)_4IBr]I$

(vi) $[Fe(NH_3)_5(CN)]SO_4$ and $[Fe(NH_3)_5SO_4]CN$.

Replaced by H_2O molecule

Ionisation isomers show different properties, *e.g.*, $[Co(NH_3)_5Br]SO_4$(I) and $[Co(NH_3)_5(SO_4)]Br$ (II) which are ionisation isomers to each other show different properties as mentioned below:

(i) (I) is red-violet while (II) is red.

(ii) When these isomers are dissolved in water, they give different ions as shown below:

Change in diff. ion

$$\underset{\text{(I) (red-violet)}}{[Co(NH_3)_5Br]SO_4} \rightleftharpoons [Co(NH_3)_5Br]^{2+} + SO_4^{2-}$$

$$\underset{\text{(II) (red)}}{[Co(NH_3)_5SO_4]Br} \rightleftharpoons [Co(NH_3)_5SO_4]^{+} + Br^{-}$$

It is due to the formation of different ions in solution that these compounds show different behaviour when treated with an aqueous solution of $BaCl_2$ and $AgNO_3$. (I). gives a *white ppt.* of $BaSO_4$ with an aqueous solution of $BaCl_2$ indicating that SO_4^{2-} ions in (I) are outside the coordination sphere. This compound does not give any ppt. with the aqueous solution of $AgNO_3$. On the other hand, (II) does not give any ppt. with a solution of $BaCl_2$ but forms a *yellow ppt*. of AgBr with $AgNO_3$ solution, indicating that Br^- ions in this compound are outside the coordination sphere.

$$\underset{\text{(I)}}{[Co(NH)_3)_5Br]SO_4} + \underset{\text{(Solution)}}{BaCl_2} \longrightarrow \underset{\text{White ppt.}}{BaSO_4} + [Co(NH_3)_5Br]Cl_2$$

$$\underset{\text{(I)}}{[Co(NH_3)_5BrSO_4} + \underset{\text{(Solution)}}{AgNO_3} \longrightarrow \text{No reaction}$$

$$\underset{\text{(II)}}{[Co(NH_3)_6SO_4]Br} + \underset{\text{(Solution)}}{BaCl_2} \longrightarrow \text{No reaction}$$

$$\underset{\text{(II)}}{[Co(NH_3)_5SO_4]Br} + \underset{\text{(Solution)}}{AgNO_3} \longrightarrow \underset{\text{Yellow ppt.}}{AgBr} + [Co(NH_3)_5SO_4]NO_3$$

It may be noted that the coordination number of the central atom in both the ionisation isomers is the same. Ionisation isomers can be detected by the determination of their conductance in solution.

Detect

3. Hydrate Isomerism

This type of isomerism is similar to ionisation isomerism. Hydrate isomers are obtained when H_2O molecules acting as ligands are replaced by the anions present outside the coordination sphere. $CrCl_3 \cdot 6H_2O$ exists in three hydrate isomers which are $[Cr(H_2O)_6]Cl_3$(I), $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ (II) and $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$ (III). These have different physical and chemical properties, e.g.,

(i) (I) is violet, does not lose water over conc. H_2SO_4 and all the three Cl^- ion are precipitated as AgCl with $AgNO_3$ solution.

$$\underset{\text{(I) (violet)}}{[Cr(H_2O)_6]Cl_3} + \underset{\text{(solution)}}{3AgNO_3} \longrightarrow \underset{\text{white ppt.}}{3AgCl\downarrow} + [Cr(H_2O)_6](N$$

or $$3Cl^- + 3Ag^+ \longrightarrow 3AgCl\downarrow$$

adia-

(ii) (II) is blue-green, loses only one H_2O molecule over olex having

Scanned with CamScanner

$CO_3(NH_3)_5$

$$\underset{\text{(II)(green)}}{[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O} + \underset{\text{(solution)}}{2AgNO_3} \longrightarrow \underset{\text{white ppt}}{2AgCl} + [Cr(H_2O)_5Cl](NO_3)_2 \cdot H_2O$$

or

$$2Cl^- + 2Ag^+ \longrightarrow 2AgCl\downarrow$$

(*iii*) (III) is blue-green, loses two H_2O molecules over conc. H_2SO_4 and only one Cl^- ion is precipitated by $AgNO_3$ solution.

$$\underset{\text{(III)(green)}}{[Cr(H_2O)_4Cl_2]Cl.2H_2O} + \underset{\text{(solution)}}{AgNO_3} \longrightarrow \underset{\text{white ppt.}}{AgCl} + [Cr(H_2O)_4Cl_2]NO_3 \cdot 2H_2O$$

or

$$Cl^- + Ag^+ \longrightarrow AgCl\downarrow$$

The behaviour of these isomers over conc. H_2SO_4 as mentioned above indicates that the number of H_2O molecules outside the coordination sphere in (I), (II) and (III) is equal to zero, one and two respectively.

The action of $AgNO_3$ solution on these isomers indicates that (I), (II) and (III) have three, two and one Cl^- ions outside the coordination sphere.

Other examples of hydrate isomers are given below:

(*i*) $[Co(en)_2(H_2O)Cl]Cl_2$ and $[Co(en)_2Cl_2]Cl \cdot H_2O$
(*ii*) $[Co(NH_3)_4(H_2O)Cl]Cl_2$ and $[Co(NH_3)_4Cl_2]Cl \cdot H_2O$
(*iii*) $[Cr(py)_2(H_2O)_2Cl_2]Cl$ and $[Cr(py)_2(H_2O)Cl_3] \cdot H_2O$
(*iv*) $[Cr(en)_2(H_2O)_2]Br_3$ and $[Cr(en)_2(H_2O)Br]Br_2 \cdot H_2O$

4. Coordination Isomerism

This type of isomerism is shown by those complex compounds which are composed of complex cation and complex anion. Coordination isomers are obtained when some or all ligands of both the coordination spheres are interchanged with each other. Thus both the complex compounds of each of the following pairs are coordination isomers to each other. In these pairs the central metallic atom in the two coordination spheres may be the same or different.

(*i*) $[Cr^{3+}(NH_3)_6]^{3+}[Cr^{3+}(CN)_6]^{3-}$ and $[Cr^{3+}(NH_3)_4(CN_2)]^+[Cr^{3+}(CN)_4(NH_3)_2]^-$
(*ii*) $[Pt^{2+}(NH_3)_4]^{2+}[Pt^{2+}Cl_4]^{2-}$ and $[Pt^{2+}(NH_3)_3Cl]^+[Pt^{2+}Cl_3(NH_3)]^-$
(*iii*) $[Co^{3+}(NH_3)_6]^{3+}[Cr^{3+}(CN)_6]^{3-}$ and $[Co^{3+}(CN)_6]^{3-}[Cr(NH_3)_6]^{3+}$
(*iv*) $[Cu^{2+}(NH_3)_4]^{2+}[Pt^{2+}Cl_4]^{2-}$ and $[Cu^{2+}Cl_4]^{2-}[Pt^{2+}(NH_3)_4]^{2+}$
(*v*) $[Cr^{3+}(NH_3)_6]^{3+}[Cr^{3+}(SCN)_6]^{3-}$ and $[Cr^{3+}(NH_3)_4(SCN)_2]^+[Cr^{3+}(SCN)_4(NH_3)_2]$

5. Linkage Isomerism

Linkage isomerism is shown by those coordination compounds which contain ambidentate ligands, (e.g., NO_2^-, SCN^-), since these ligands can coordinate to the central metal atom through any of the two different available donor atoms. The linking of ambidentate ligand to the metal atom through two different donor atoms gives two different compounds which are related with each as linkage isomers. Examples of linkage isomers are:

NH_3

NO_2

(*i*) $[Co^{3+}(NH_3)_5NO_2]^{2+}$ (I) and $[Co^{3+}(NH_3)_5ONO]^{2+}$ (II) are linkage isomers. In (I), NO_2^- ligand is linked with Co^{3+} ion through its N-atom while in (II), NO_2^- … through its O atom. (I) is called *penta ammine-*

---

nitro (NO_2) Yellow : nitrito (ONO) Red.

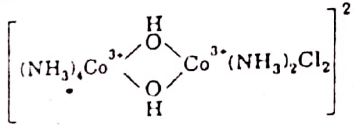
nitro cobalt (III) ion while (II) is called *pentaamminenitrito cobalt (III) ion.*

(I) is yellow while (II) is red.

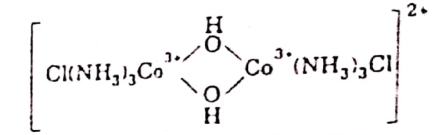
(*ii*) $[Pd^{2+}(dipy)(SCN)_2]^\circ$ (orange yellow) and $[Pd^{2+}(dipy)(NCS)_2]^\circ$ (light yellow) are linkage isomers. First compound is called *dipyridyldithiocyanato palladium (II)* while the second compound is called *dipyridyl diisothiocyanato palladium (II).*

6. Coordination Position Isomerism

This type of isomerism is shown by those complex compounds which contain bridging ligands and arises when the non-bridging ligands are differently placed round the central metal atom. Thus (I) and (II) are coordination position isomers to each other, since NH_3 molecules and Cl^- ions (non-bridging ligands) are differently placed round the two Co^{3+} ions.

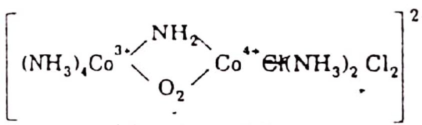


Tetrammine coblat (III) μ-dihydroxo diammine dichloro cobalt (III) ion. (I) (*unsymmetrical*)

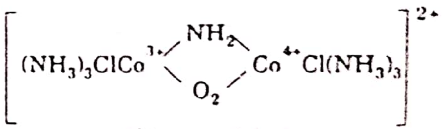


Chloro triammine cobalt (III) μ-dihydroxo chloro triammine cobalt (III) ion. (II) (*symmetrical*)

The following binuclear complexes of cobalt also show coordination position isomerism, since the terminal ligands, viz., six NH_3 molecules and two Cl^- ions can be placed in an unsymmetrical and symmetrical manner round the central cobalt atom.



(*a*) unsymmetrical



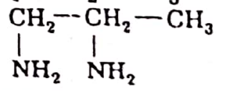
(*b*) symmetrical

7. Ligand Isomerism

There are certain ligands which exist as isomers, e.g., diamine derivatives of propane exist in two isomeric forms which are called 1, 2-diamino propane or propylene diamine (*pn*) and 1, 3-diamino propane or trimethylene diamine (*tn*). The structures of propane, *pn* and *tn* are given below:

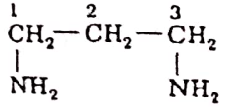
$$\overset{1}{C}H_3-\overset{2}{C}H_2-\overset{3}{C}H_3$$

Propane



$$\underset{NH_2}{\overset{1}{C}H_2}-\underset{NH_2}{\overset{2}{C}H}-\overset{3}{C}H_3$$

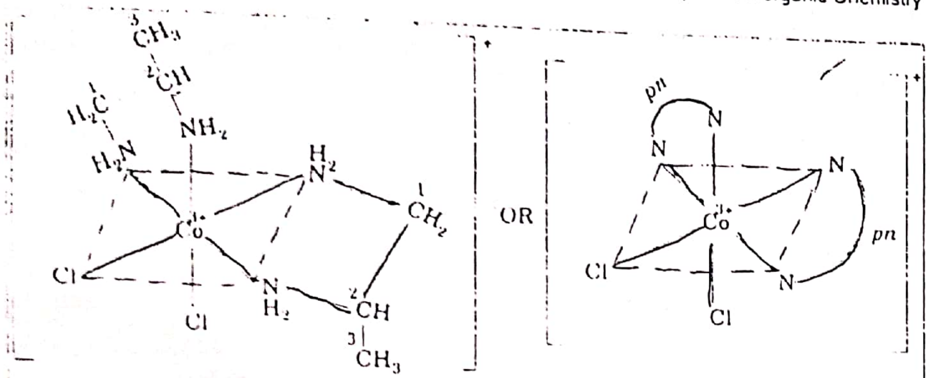
1, 2-diamino propane or propylene diamine (*pn*)



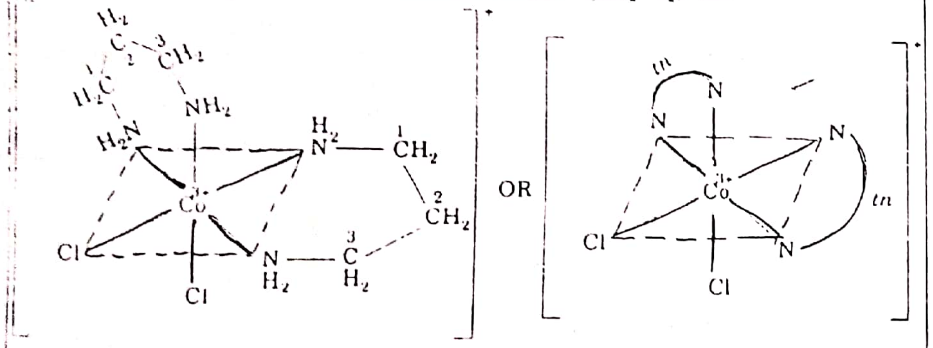
$$\underset{NH_2}{\overset{1}{C}H_2}-\overset{2}{C}H_2-\underset{NH_2}{\overset{3}{C}H_2}$$

1, 3-diamino propane or trimethylene diamine (*tn*)

pn and *tn* both are bidentate (neutral) ligands. When these ligands get coordinated to the metal atom, two isomers are obtained. These are called ligand isomers and the isomerism is called ligand isomerism. Thus $[Co^{3+}(pn)_2Cl_2]^+$ and $[Co^{3+}(tn)_2Cl_2]^+$ are ligand isomers whose structures are given below in Fig. 15.1. Both these isomers



(a) Structure of $[Co^{3+}(pn)_2Cl_2]^+$ ion



(b) Structure of $[Co^{3+}(tn)_2Cl_2]^+$ ion.

Fig. 15.1. Structures of $[Co(pn)_2Cl_2]^+$ and $[Co(tn)_2Cl_2]^+$ ions.

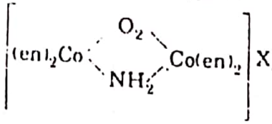
8. Polymerisation Isomerism

This type of isomerism is found in those complex compounds whose formulae appear to be polymers of some simple complex compound. All these complex compounds have the same ratio of different metal atoms and ligands in them. For example, the following complex compounds are polymerisation isomers to each other, since (*ii*) and (*iii*) complxes appear to be dimer of (*i*) complex and (*iv*) complex appears to be the pentamer of (*i*) complex. The ratio Co^{3+} : NH_3 : NO_2^- in all the complexes is 1 : 3 : 3.

	Complex compound	Co^{3+}	*Number of* NH_3	NO_2^-
(*i*)	$[Co(NH_3)_3(NO_2)_3]$	1	3	3
(*ii*)	$[Co(NH_3)_6][Co(NO_2)_6]$	2	6	6
(*iii*)	$[Co(NH_3)_4(NO_2)_2][Co(NH_3)_2(NO_2)_4]$	2	6	6
(*iv*)	$[Co(NH_3)_5(NO_2)]_3[Co(NO_2)_6]_2$	5	15	15

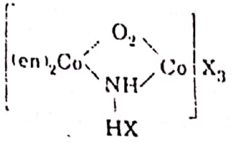
9. Valency Isomerism

This isomerism arises when the ligand is held by different types of valency bonds, sometimes primary or secondary. For example:



$[(en)_2Co(O_2)(NH_2)Co(en)_2]X_4$

and



$[(en)_2Co(O_2)(NH\cdot HX)Co]X_3$

Stereo Isomerism

Stereo isomerism is exhibited by those compounds which have the same position of atoms or groups but these atoms or groups have different arrangement round the central atom. The compounds showing stereo isomerism are called **stereo isomers**. Stereo isomerism may be of two types *viz. geometrical (or cis-trans) isomerism* and *optical (or d-l or mirror-image) iosmerism*.

Geometrical (or cis-trans) Isomerism

The complex compounds which have the same ligands in the coordination sphere but the relative position of the ligands round the central metal atom is different are called *geometrical isomers* and the phenomenon is called *geometrical isomerism*.

In a given complex compound the two ligands may occupy positions either adjacent to each other or opposite to each other. The complex compound having two ligands occupying the adjacent positions to each other is called *cis-isomer* while that in which the two ligands occupy opposite positions is called *trans-isomer*. Hence geometrical isomerism is also called *cis-trans isomerism*.

Geometrical isomers of a complex differ in physical characteristics such as dipole moment and visible / uv spectra.

Geometrical Isomerism in Complexes with C.N. 2 and 3

Geometrical isomerism is not found in complex compounds with coordination number 2 and 3, since in these cases all the positions occupied by the ligands round the central metal atom are adjacent to one another.

Geometrical Isomerism in Tetrahedral Complexes (C.N. = 4)

Geometrical isomerism cannot be shown by tetrahedral complexes, since all the four ligands in this geometry have adjacent position (*i.e.*, *cis* position) to one another and all the four bond angles are the same (= 109.5°).

Geometrical Isomerism in Square Planar Complexes (C.N. = 4)

Before discussing the geometrical isomerism exhibited by various types of square planar complexes, we should know how *cis* and *trans* isomers of a square planar complex are named. A square planar complex having similar ligands at adjacent positions (90° apart) is called *cis*-isomer while a square planar complex having